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LC/MS Application Note

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Two Sources are Better Than One – More Choices for Sample Ionization with ESI and APCI

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Introduction

Two compounds were submitted for molecular weight determination using the 1200L LC/MS. Electrospray Ionization (ESI) is generally the ionization method of choice for compounds analyzed with LC/MS systems. ESI works well for a wide variety of analytes. However, there are instances where particular analytes do not ionize well with ESI. In these cases, a second ionization method, Atmospheric Pressure Chemical Ionization (APCI), may often give the needed sensitivity.

While both positive ESI and APCI can result in a charged analyte, the process of ionization is very different. With ESI, protonation of the analyte occurs in liquid phase. With APCI, a protonated solvent molecule donates a proton to the analyte in the gas phase.

In general, APCI is better suited for ionization of non-polar, volatile low molecular weight molecules while ESI is better suited for more polar, non-volatile molecules.

Instrumentation

- Varian 1200L LC/MS equipped with ESI and APCI sources
- Harvard Apparatus Pump 11 Syringe Pump

Materials and Reagents

- Compound 1: an extended aromatic ring system with an amine, molecular formula not provided, MW = 451.
- Compound 2: an aliphatic amide with an amine aliphatic benzyl ether chain having the molecular formula $C_{33}H_{44}N_2S_2O_4$, MW = 596.1.
- Both compounds were provided as solids and were dissolved in HPLC grade reagents to give a ~1.0 µg/mL (1 ppm) concentration solution for direct infusion into the mass spectrometer.
- Syringe Pump Conditions: Flow Rate: 10 µL/min (10 ppm) for ESI, 20 µL/min (20 ppm) for APCI. Solvent Composition: 50:50 Methanol:0.1% Formic acid.

MS Parameters

ESI	
API Drying Gas	21 psi at 225 °C
API Nebulizing Gas	51 psi
Scan Time	0.25 sec
SIM Width	0.7
Needle	5000V
Shield	600V
Capillary	50V
Detector	1500V

MS Parameters

APCI	
API Drying Gas	15 psi at 150 °C
API Nebulizing Gas	60 psi
API Auxiliary Gas	17 psi at 350 °C
Corona Discharge	5 µA
Needle	5000V
Shield	600V
Capillary	50V
Detector	1500V

Results and Discussion

The ESI molecular ion scan for Compound 1 is shown in Figure 1. The protonated molecular ion $(M+H)^+$ is observed at m/z = 452.1 as expected. Conversely, when Compound 1 is infused into the APCI source, Figure 1, a very weak molecular ion is observed at the expected m/z = 452.1 when compared to the ESI conditions. Negative ionization yielded no molecular ion in either APCI or ESI mode.

Molecular Ion Spectra – Compound 1

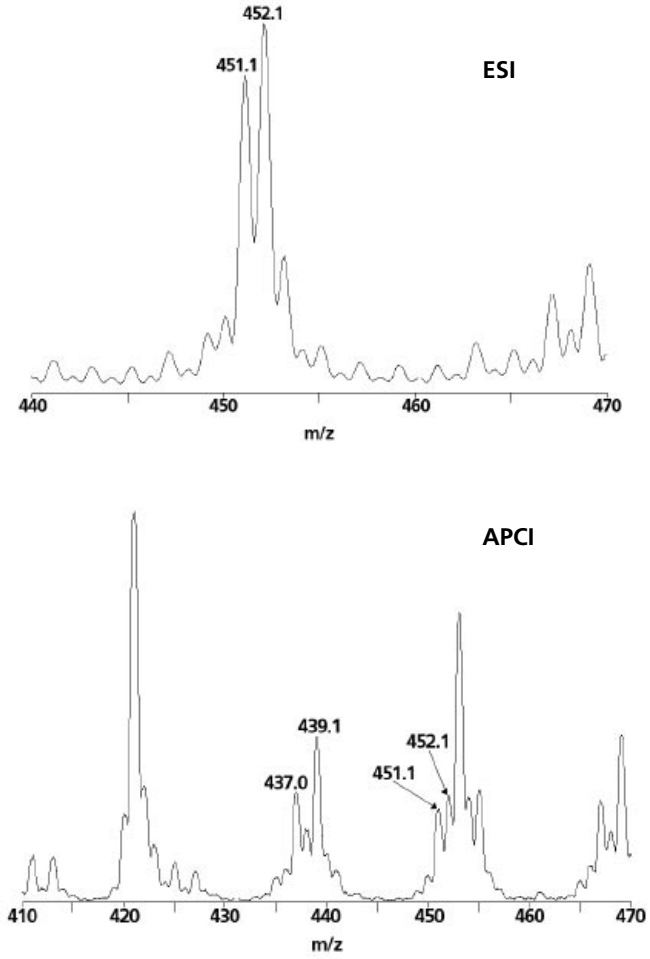

Figure 1. ESI produces excellent molecular ion signal for Compound 1, while APCI does not.*

*As the molecular formula was not provided for the molecule, the cluster of ions associated with the molecule cannot be assigned, for example, the presence of isotopes within the structure.

The ESI molecular ion scan for Compound 2 is shown in Figure 2. At the expected m/z ratio for the protonated molecule, 597.1, no signal is observed. However, when switching the ionization source from the ESI to APCI, a distinct molecular ion peak is observed at m/z = 597.1 in Figure 2.

Molecular Ion Spectra – Compound 2

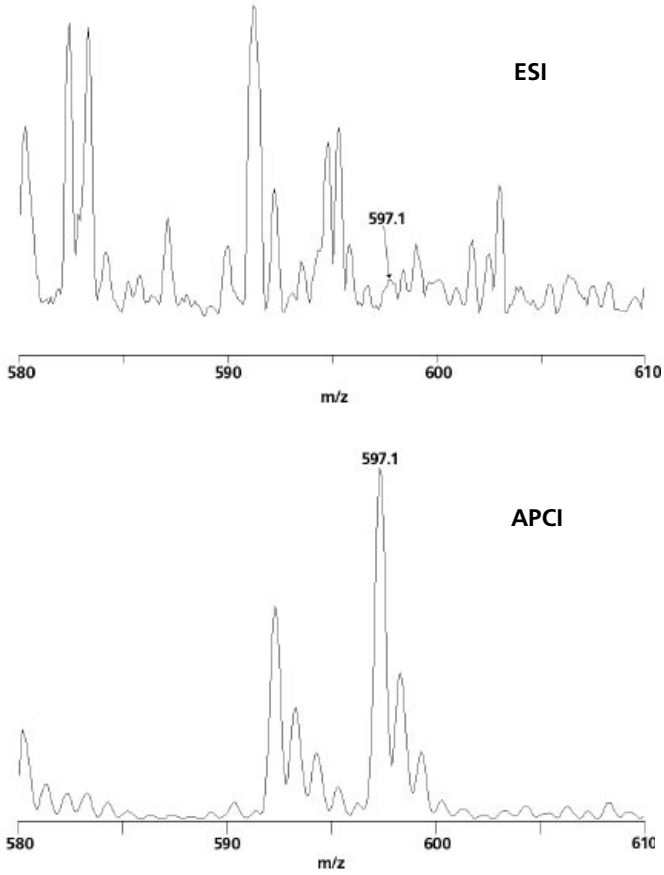

Figure 2. APCI produces excellent molecular ion signal for Compound 2, while ESI does not.

Conclusion

A wide variety of analytes can be routinely analyzed using the Varian 1200L LC/MS system. However, one ionization source may not provide the information for the analyte of interest based on its characteristics and various mobile phase conditions. By having access to both ionization methods, ESI as well as APCI, the ability to ionize different analytes greatly increases.

These data represent typical results.
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